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## Abstract

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## KINETIC FEATURES OF THE LIQUID-PHASE AUTOOXIDATION OF ISOPROPYLXYLENES

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As was shown earlier ([1]), the autooxidation of polyalkylbenzenes that do not contain alkyl groups in the *o*-position relative to one another is a strictly consecutive reaction.

In continuation of this study, it was of interest to investigate the kinetic regularities of the autooxidation of polyalkylbenzenes having substituents located adjacent to one another. The following compounds were selected as objects: *o*-xylene (I), 4-isopropyl-*o*-xylene (II), 3-isopropyl-*o*-xylene (III), 2-isopropyl-*p*-xylene (IV), 4-isopropyl-*m*-xylene (V), 2,5-diisopropyl-*p*-xylene (VI), and *o*-cymene (VII).

It was established that during the autooxidation of all the above hydrocarbons, along with the usual products (alcohols, ketones, acids, etc.), $\gamma$-lactones—phthalide derivatives—are also formed. The formation of the latter under conditions of liquid-phase autooxidation was observed by us for the first time. (I) at 120° in the presence of 0.6 mol.% cobalt acetate is oxidized in 8–10 hr by 60–70%. In this process, along with the main reaction product—*o*-toluic acid—5–8% phthalide and 2–5% of a mixture of tolualdehyde and tolylcarbinol are formed. The maximum concentration of hydroperoxide does not exceed 1–1.5%. (II), upon oxidation, forms a rather complex mixture. In the early stages of autooxidation the isopropyl group reacts with peroxide radicals 1.8–2.1 times faster than the two methyl groups. Of the latter, the radical located in the *p*-position to the isopropyl group is oxidized approximately 1.2 times more readily. The influence of various factors on the course of oxidation of (II) is given in Table 1. As is seen from the data of Table 1, the yield of lactones is approximately 5% of the oxidized hydrocarbon. Other products with two oxidized groups (acetyl-$\alpha$-oxyisopropyltoluic acids, etc.) are formed in appreciable amounts at an oxidation depth greater than 30%.

**Table 1**

**Autooxidation of 4-isopropyl-*o*-xylene**

| No. | Resinous substances, mg | Soda, g | Temp., °C | Hydroperoxide conc., % (above line); time, hr (below line) | Hydrocarbon | Dimethylphthalide | [illegible] | Isopropyltoluic acid | [illegible] | Isopropylphthalide | Other products with two oxidized groups |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 10 | 1.5 | 120 | 8.4/1;<br>18.0/4;<br>16.5/6 | 66.4 | 14.1 | 6.3 | 5.5 | 6.0 | 1.0 | 0.7 |
| 2 | 6 | 3.0 | 110 | 12.5/2;<br>29.0/6;<br>23.0/9 | 51.2 | 22.8 | 6.9 | 11.5 | 2.5 | 2.2 | 2.9 |
| 3 | 4 | 3.5 | 110 | 9.4/1;<br>15.1/2 | 82.8 | 11.3 | 0.2 | 1.9 | 3.2 | 0.6 | — |
| 4 | 5 | 4.0 | 100 | 5.3/3;<br>12.0/7;<br>16.3/10 | 71.8 | 13.8 | — | 2.3 | 3.6 | 0.5 | — |
| 5 | 170 | — | 110 | 7.0/1;<br>4.02;<br>1.2/4 | 21.5 | 24.6 | 21.0 | 17.1 | 6.2 | 4.1 | 5.6 |

**Note.** In experiment 5 cobalt acetate was used.

The autoxidation of hydrocarbons (III)—(VII), which have methyl and isopropyl groups located next to one another, proceeds most interestingly. In the presence of manganese resinate, (III)—(V) oxidize very slowly. The use of cobalt acetate and isopropyltoluylate as initiators made it possible to accelerate the oxidation considerably; however, it was not possible to direct the process toward predominant formation of hydroperoxides, since the latter decompose very rapidly in the presence of cobalt salts. (VI), with 6 mg/mole of manganese resinate and 10 mg/mole of sodium hydroxide, was oxidized at 110° in 7 h to a hydroperoxide concentration of 10%.

If in (II) the isopropyl group is oxidized almost 4 times more readily than the methyl group, then in (IV) and (V), owing to steric hindrance, the overall oxidation rate of the two adjacent groups exceeds the oxidation rate of the isolated methyl group by only 1.3—1.7 times. It is interesting to note that *p*-xylene at 120° oxidizes only 1.3 times more poorly than (IV). (The ratio of rates was established in the co-oxidation of the hydrocarbons.) Fig. 1 presents the kinetics of the oxidation products of 4-isopropyl-*m*-xylene (V) at 130° in the presence of 1 mole % cobalt isopropyltoluylate and an air feed rate of 1 l/min, and of 2-isopropyl-*p*-xylene (IV) at 160° with 1 mole % cobalt isopropyltoluylate and an air feed rate of 1 l/min. The composition of the oxidation products of (IV) and (V) for several experiments is shown in Fig. 1 and in Table 2. From these data it is evident that lacto-

**Fig. 1.** Kinetics of accumulation of oxidation products of V (A) and IV (B): 1 –acids, 2 –total amount of lactones, 3 –trimethylphthalide, 4 –ketones, 5 –primary alcohols, 6 –tertiary alcohols, 7 –hydroperoxides

**Table 2**

**Autoxidation of 2-isopropyl-*p*-xylene and 4-isopropyl-*m*-xylene**

| No. | Isopropyltoluylate of cobalt introduced, mole % | Temp., °C | Hydroperoxide concentration, % (above line), time, h (below line) | Reaction time, h | Trimethylphthalide | Other lactones | Isopropyltoluic acids | Dimethylphenylcarbinol | Dimethylacetophenone | Isopropylbenzyl alcohol | Unreacted hydrocarbon (mole %) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | – | 110 | 1.2/5; 3.5/12; 1/24 | 24 | 4.8 | 0.8 | 8.3 | 2.9 | 2.0 | 2.6 | 70.2 |
| 2 | 0.6 | 110 | 2.0/1; 3.8/3; 1.6/9 | 9 | 14.0 | 2.1 | 20.5 | 4.2 | 3.5 | 5.0 | 46.5 |
| 3 | 1.5 | 115 | 1.3/4; 1.7/6; 0.5/14 | 14 | 12.6 | 3.0 | 25.8 | 2.7 | 4.1 | 3.3 | 42.0 |
| 4 | 1.0 | 125 | 0.6/1; 0.9/2 | 2 | 5.1 | 1.2 | 4.3 | 2.9 | 1.8 | 1.9 | 77.6 |
| 5 | 1.0 | 160 | 0.3/1; 0.4/3; 0.3/7 | 7.5 | 18.1 | 7.5 | 27.0 | 2.5 | 6.7 | 1.7 | 21.0 |
| 6 | 1.2 | 140 | 0.4/2; 0.5/3.5 | 3.5 | 15.2 | 4.0 | 21.2 | 3.2 | 5.9 | 4.1 | 39.0 |

**Notes.** 1. In experiments 1–4, (IV) was oxidized; in 5–6, (V). 2. In experiment 1, 10 mg per 1 mole of manganese resinate and 3 g per 1 mole of sodium hydroxide were taken.

are formed at a considerable rate already in the very early stages of the reaction.

In the oxidation of (VI), more than 50% lactones are formed. High yields of lactones are also obtained in the oxidation of diisopropyl-*m*-xylenes, (III) and (VII). If the oxidation of the indicated hydrocarbons proceeded as an ordinary consecutive process, then, as is readily seen with the aid of the kinetic equations (1), the formation of such considerable amounts of lactones would be possible only under the condition that the rate of oxidation of the second group exceeded the rate of oxidation of the hydrocarbon many times over. However, by special experiments we established that substances with one oxidized alkyl group, from the further oxidation of which lactones could be obtained, are less reactive than the hydrocarbon. Additions to (IV) of dimethyl-*p*-xylylcarbinol (VIII), 2-acetyl-*p*-xylene (IX), a mixture of isopropyl-*p*-toluic acids, and other products isolated from the reaction mass do not appreciably increase the yield of lactones.

Oxidation of a mixture of (VIII), (IX), and *p*-xylene showed that the oxidation rates of these compounds are close. In addition, it was observed that the yield of lactones does not increase in parallel with the concentration of hydroperoxides.

All the foregoing makes it possible to regard the presence of isomerization of free radicals as the principal reason for the formation of high yields of lactones. For example:

[[chemical structure: aromatic ring bearing $CH_3$ and $C(CH_3)_2O \cdot n$]] $\longrightarrow$ [[chemical structure: aromatic ri

$$n = 1 \text{ or } 2 \qquad (A)$$

Since a benzyl-type radical (A) practically cannot abstract a hydrogen atom from surrounding molecules, because the latter reaction for such radicals proceeds $10^5$–$10^6$ times more slowly than the addition of oxygen [2], almost every act of isomerization will lead to the formation of products with two oxidized neighboring groups.

In addition to derivatives of 3,3-dimethylphthalide, other substances are also obtained in the oxidation of (III)–(VII), the chemical properties of which are identical to those of phthalides. We were unable to isolate them as individual compounds. However, there is no doubt that these substances were formed through the autoxidation of two neighboring alkyl groups, since upon oxidation with alkaline $KMnO_4$ they gave 4-methyl-*o*-phthalic acid. Compounds of the lactone type were also obtained by us in the autoxidation of (IX) in a yield of 20–28% based on oxidized product.

## Experimental Part

Isopropylxylenes were obtained by alkylation of the corresponding xylenes with propylene in the presence of $BF_3 \cdot H_3PO_4$, or with isopropyl alcohol in the presence of 85% $H_2SO_4$. (VIII) was obtained by Grignard reaction from 2-bromo-*p*-xylene; (IX) was synthesized from *p*-xylene and acetyl chloride in the presence of $AlCl_3$. The starting xylenes were chemically pure commercial preparations. The hydrocarbons were thoroughly purified by rectification on a column of 25 –30 theoretical plates and had constants corresponding to the literature data. (VII) was used as a mixture of isomers containing about 40% *o*-cymene.

Autoxidation was carried out as before [1], but a calibrated trap was used to determine the amount of water evolved. During the course of the reaction, samples were taken in which the contents of hydroperoxides, acids, primary and tertiary alcohols, unsaturated compounds, ketones, keto acids, and lactones were determined. The determination of lactones was based on the fact that the alkaline salts of the oxy acids obtained upon saponification pass quantitatively, upon heating in an acidic or even weakly alkaline medium, into neutral lactones. (Derivatives of 3,3-dimethylphthalide are readily formed in a weakly alkaline medium, whereas phthalide and compounds similar to it are formed in an acidic medium.)

Tertiary alcohols were determined by dehydration in the presence of $KHSO_4$, followed by titration of the water with Fischer reagent. The remaining compounds were analyzed by the usual methods. When titration with indicators was difficult, potentiometric titration was carried out.

The composition of the isomeric isopropyltoluic acids was established as follows. The acids were decarboxylated almost quantitatively in the presence of copper powder in quinoline; the mixture of cymenes was oxidized with dilute $HNO_3$ in an autoclave to phthalic acids, which were separated through barium salts or on the basis of their different solubilities in water. It was thus established that oxidation of (II) gives about 55% 4-isopropyl-*o*-toluic acid (m.p. 89°) and 45% 5-isopropyl-*o*-toluic acid. The mixture of acids obtained by oxidation of (IV) and (V) contains, respectively, 80% 3-isopropyl-*p*-toluic acid (m.p. 147°) and 75% 4-isopropyl-*m*-toluic acid (m.p. 128°). Approximately the same ratios also occurred among the isomeric isopropylxylylcarbinols, which were isolated from the mixture with the aid of complex esters and converted into acids, or directly into cymenes, by heating with caustic potash ([3]).

The acids were isolated from the reaction mass with the aid of soda (lactones do not dissolve in soda). In isolating the lactones, various methods were used (extraction with caustic alkali, rectification, and crystallization). We succeeded in obtaining in pure form and identifying the following lactones. Phthalide (X), m.p. 75°; 3,3-dimethylphthalide (XI), m.p. 69.5°; 3,3,5-trimethylphthalide (XII), m.p. 92°, b.p. 297°; 3,3,6-trimethylphthalide (XIII), b.p. 294°, $n_D^{20}$ 1.5280, $d_4^{20}$ 1.087; 3,3,7-trimethylphthalide (XIV), m.p. 60.5°; 3,3,5-trimethyl-6-isopropylphthalide (XV), m.p. 85°, b.p. 165°/10 mm.

Mixed samples of (X) and (XI) with definitely pure specimens gave no depression. The structures of (XIII) and (XIV) were proved by their oxidation with alkaline $KMnO_4$ to acids. 3,3-Dimethylphthalidecarboxylic-6-acid had m.p. 204°, and

3,3-dimethylphthalidecarboxylic-7-acid 185°, which agrees with the literature data (4, 5). (XII) was oxidized with nitric acid to trimellitic acid and converted by heating with KOH into *n*-toluic acid and acetone.

The structure of the dimethylacetophenones was confirmed by obtaining semicarbazones and 2,4-dinitrophenylhydrazones. The tertiary alcohols were not isolated in pure form. Their structure was proved by conversion into the corresponding trimethylstyrenes, which we oxidized with permanganate to dimethylacetophenones or dimethylbenzoic acids.

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